Metal-induced gap states in epitaxial organic-insulator/metal interfaces

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We have shown, both experimentally and theoretically, that the metal-induced gap states (MIGS) can exist in epitaxially grown organic insulator/metal interfaces. The experiment is done for alkane/Cu(001) with an element-selective near edge x-ray absorption fine structure (NEXAFS), which exhibits a pre-peak indicative of MIGS. An *ab initio* electronic structure calculation supports the existence of the MIGS. When the Cu substrate is replaced with Ni, an interface magnetism (spin-polarized organic crystal at the interface) is predicted to be possible with a carrier doping.

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Introduction While there are mounting interests in the nature of heterointerfaces (solid-solid interfaces between very dissimilar materials), organic crystal/metal interfaces are especially intriguing due to their diverse possibilities not found in inorganic counterparts, which may facilitate in controlling and designing properties of interfaces. Electronic structures of organic/metal interfaces are important from a technological point of view as well, since the performance of devices should strongly depend on the electronic structure at the interface.

Recent years have in fact witnessed several interesting results on the electronic structure of various organic-crystal/metal interfaces. While it is well-known that a bulk C_{60} crystal becomes a superconductor when doped with alkali metals [1], a charge transfer was also observed for C_{60} crystal grown on metal substrates [2]. Cepek *et al.* went further to suggest that a temperature-dependent gap structure around Fermi energy for a single-crystal C_{60} film on Ag(001) may possibly be superconductivity induced by the charger transfer [3]. Lukas *et al.* on the other hand observed a charged-density wave in an ordered pentacene film on Cu(110) and its effect on the crystal growth [4].

One crucial factor in such organic-insulator/inorganic-metal heterointerfaces is the energy level alignment at the interface, which is still far from fully understood. The band alignment, measured by photoelectron spectroscopy and Kelvin probe, has been discussed in terms of various effects, such as electron transfer, image effect, modification of the surface dipole at metal surface, chemical interaction and interfacial states [5]. However, there is no generally accepted picture for organic/metal interfaces, which is contrasted with inorganic-semiconductor/metal interfaces where the band alignment is known to be governed by the interface states called the metal-induced gap states (MIGS) [6]. So a study of the interface states at the organic/metal interfaces should be imperative.

The notion of MIGS was first introduced for semiconductor/metal junctions in discussing the Schottky barrier [6]. MIGS are roughly free-electron-like metal wave functions penetrating into the semiconducting side, where the penetration depth is inversely proportional to the band gap in the conventional band picture. So a usual wisdom is that MIGS would be far too thin in insulator/metal interfaces to be relevant. The present authors succeeded in fabricating epitaxial alkali halide(insulator)/metal interfaces, which has enabled us to obtain unambiguous evidences especially from the near edge x-ray absorption fine structure (NEXAFS) that MIGS are in fact formed at the inorganic insulator/metal interfaces [7,8].

While alkali halides are typical ionic insulators, interface states for *organic*-insulator/metal interfaces are a totally different issue, since chemical bonds of organic insulators are covalent, and it is a fundamental question to ask whether the formation of MIGS at insulator/metal interfaces are universal enough to accommodate organic insulators. Experimentally, interface states in atomically well-defined organic-insulator/metal interfaces has yet to be observed to our knowledge [9], despite the prime importance. One obvious reason for this is difficulties in fabricating atomically well-defined organic-insulator/metal interfaces and in detecting signals from the interface [7]. However, recent developments in the molecular beam epitaxy (MBE) technique have made it possible to prepare various types of heterointerfaces in case of inorganic materials [10], and novel electronic structures including MIGS are revealed at the interfaces [7]. On the other hand, some organic films are begun to be epitxially grown on metal substrates in a layer-by-layer fashion with MBE [11,12].

Given this background, the purpose of this Letter is to examine the interface states in an atomically well-defined organic insulator ($C_{44}H_{90}$) grown on Cu substrate. We have found, with the element-selective NEXAFS, a pre-

peak indicative of metal-induced gap states. At the same time we have performed an *ab initio* electronic structure calculation. The theoretical result shows that (i) MIGS do exist at the organic insulator/metal interface, and (ii) when we replace Cu with Ni, in which narrow 3d bands rather than wide 4s bands dominate the electronic properties around the Fermi energy, an interface magnetism (spin-polarized organic crystal at the interface) is predicted to be possible with a carrier doping.

Experimental The experiments were performed with a UHV chamber at the soft x-ray beam line BL-7A in the photon factory in the Institute of Materials Structure Science, Tsukuba, Japan. We have employed an alkane (C_nH_{2n+2} with $n = 44$; tetratetracontane or TTC), where the properties of this series of molecules are similar except for a variation of the band gap with n. TTC was evaporated on Cu(001) with the substrate temperature of 300 K in a Knudsen cell. Real-time observation of crystallinity and orientation of the molecules was done with the reflection high energy electron diffraction (RHEED). A clear RHEED pattern is observed for 1 monolayer (ML) thick TTC/Cu(001). This indicates that the TTC film epitaxially grows on Cu(001) with its molecular axis parallel to the [110] azimuth of the Cu substrates in a layer-by-layer fashion [12]. Carbon K-edge NEXAFS spectra were then obtained by the partial electron yield method with a micro-channel plate.

Figure 1 shows the NEXAFS for a 1ML TTC on Cu(001), as compared with the result for a bulk (multilayer) TTC film. A broad peak at about 293 eV can be assigned to C 1s to σ^*(C-C) resonance, while the peak at 288 eV to a C 1s to σ^*(C-H) [13]. There are two points to note in the result for 1ML TTC/Cu(001). First, the NEXAFS result exhibits a clear polarization dependence. The σ^*(C-C) peak, whose transition moment is parallel to the -C-C-C- plane, is most enhanced at the normal x-ray incidence, which confirms that the TTC grows on Cu(001) with its molecular axis parallel to the substrate. On the other hand, the σ^*(C-H) peak, whose transition moment $\perp$ -C-C-C- plane, splits into two. This should be because one-half of the hydrogen atoms in the organic molecule touch the substrate in the lying-down configuration as depicted in an inset in Fig. 2, so that the (C-H) state splits due to the interaction between TTC and Cu [13].

More importantly, a pronounced pre-peak is seen to appear below the bulk edge onset, and this indicates a first observation of the interface states at the organic insulator crystal/metal interface. Because the adsorption energy of alkanes on metal surfaces is small (~ 10 kJ/mol/CH_2 chain), the nature of the chemical bond at the interface should be a typical physisorption state with a weak molecule-surface interaction, as contrasted with a chemisorption with chemical bonds formed at the interface. So the pre-peak originates from the proximity to a metal rather than from chemical bonds, and we have

here an evidence for the formation of MIGS at an organic insulator/metal interface.

The right panel of Fig. 1 is a blowup of the absorption edge for 1ML TTC/Cu(001). We can see that the pre-peak is greater for a grazing x-ray incidence than for the normal incidence. In NEXAFS, the electronic state whose wave function orients in the surface normal direction is selectively detected for grazing x-ray incidence, so the result indicates that the MIGS wave functions are oriented in the surface normal direction.

Ab-initio calculation Let us now move on to the first-principles (density functional theory) calculation for the heterointerface to explore the electronic structure, especially the MIGS, and to see how the above experimental result fits the theoretical picture. Quite recently Morikawa *et al.* [14] have performed a first principles calculation for interfaces between alkane and various metals such as Cu, where the change in the work function and a softening of the CH stretching mode have been studied. Here we explore the local density of states, and also study what will happen when we replace the substrate with a *ferromagnetic* d-band metal such as Ni, for which the spin-density functional theory is employed. Our expectation for such a case is the following: The density of unoccupied states of Ni substrate should be much greater than that of Cu, because Ni is ferromagnetic (spin polarized) with the major part of the minority-spin 3d band sitting above the Fermi energy. So, naively, the intensity of MIGS for organic/Ni would be much stronger than that for organic/Cu.

A penalty for doing a first-principles band calculation is, given the complexity of the system, we have to replace the alkane with a finite n with polyethylene, which is assumed to be infinitely long. This reduces the size of the unit cell, enabling us to perform the spin density functional study. We have also assumed that polyethylene chains are close-packed, while an experiment [12] for TTC indicates that the real packing has half this density. We adopt the exchange-correlation functional introduced by Perdew *et al.* [15] and employ ultra-soft pseudopotentials in separable forms [16,17]. The cut-off energy of the plane-wave expansion for the wave function is taken to be 42.25 Ry. The atomic configurations (inset of Fig. 2) and the corresponding electronic ground states are obtained with the conjugate gradient scheme [18].

Figure 2 shows the band structure along with the local density of states (LDOS) for polyethylene/Cu. The LDOS at E_F is calculated as $\sum_i |\phi_i(x,y,z)|^2$ with the summation taken over the eigenstates (labeled by i) having energies $E - 0.125\text{eV} < E_i < E + 0.125\text{eV}$. The number of sampled k points is 8 with the Monkhorst-Pack method for the integration over the Brillouin zone [19], where the bands are fitted to sinusoidal forms and the tetrahedron method is employed. We can see in the result that LDOS at E_F has a peak on the carbon site, which indicates that MIGS are formed at the polyethy-

lene/Cu interface. The wave function contour (inset of Fig. 2) confirms this in the three-dimensional space.

Ni substrate If we now come to polyethylene/Ni in Fig. 3, we have to look at the majority- and minority-spin components separately, since the Ni substrate is spin polarized. We can see that the local density of states around E_F significantly differs between the majority and minority spins, including those at the carbon sites. In the energy-resolved LDOS (color-coded panel in Fig. 3) this is seen to come from a difference in the position of MIGS in the occupied ($E < E_F$) side. To be more precise, there is a finite exchange splitting for the MIGS in polyethylene/Ni interface, although the splitting is smaller than the splitting within the Ni substrate. However, both the majority- and minority-spin MIGS lie below the E_F (with the latter lying just below E_F). This implies that the organic crystal, although lying on a ferromagnetic substrate, is not spin-polarized. Figure 4 compares for Ni and Cu substrates the total (i.e., sum of the majority- and minority-spin) LDOS (which is relevant to the NEXAFS). In accord with the above, the density of unoccupied MIGS states is similar between polyethylene/Ni and polyethylene/Cu, while the density of occupied MIGS states differs between them because the 3d band resides just below E_F for Ni. The theoretical prediction agrees with our preliminary NEXAFS result, a probe for unoccupied states, for octane(C_8H_{18}) on Ni(111) and Cu(111) substrates. The intensity of pre-peak is similar between the two systems, with the intensity normalized by the edge jump being 0.27 for octane/Ni(111) against 0.30 for octane/Cu(111).

We can summarize the band scheme in Fig. 5, which schematically depicts the energy regions for MIGS in the organic/Cu and organic/Ni interfaces. The MIGS band for the majority spin in polyethylene/Ni lies below E_F, so the density of states in the unoccupied side is small, while the density of occupied states is large. By contrast, E_F runs right through the MIGS band when the substrate is Cu, but the density of MIGS is relatively low due to a low density of states of the Cu 4s band. This results in little difference between organic/Ni and organic/Cu as far as the density of *unoccupied* MIGS is concerned, so an experimental method that detects occupied states, such as resonant photoemission or x-ray emission spectroscopy, will probe the difference.

While the spin-*un*polarized MIGS on a ferromagnetic substrate is a bit of a disappoinment, the above picture naturally leads us to the following theoretical proposal. In the energy diagram in Fig.5, we can make the MIGS spin-*polarized* if we can introduce carriers into MIGS by, e.g., chemical doping. Namely, while normally the majority and minority spins are (almost) fully occupied in organic/Ni, the doped carriers will accommodated in the minority-spin band as indicated by a dashed line in Fig.5, so that we should end up with a polarized organic molecules.

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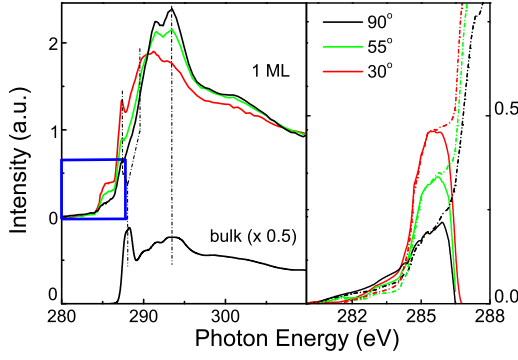[19] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

FIG. 1. Experimental result for the C-K edge NEXAFS spectra in 1 ML $C_{44}H_{90}$(TTC) films grown on Cu(001) for the x-ray incidence angle θ varied over $30°$, $55°$, $90°$. We also show for comparison the result for a multilayer TTC (bulk) on Cu(001) in black (which is almost θ-independent but displayed here for $\theta = 90°$). All the spectra are normalized by their edge-jump. Right panel is a blowup of the prepeaks, obtained by subtracting the bulk (multilayer) spectrum.
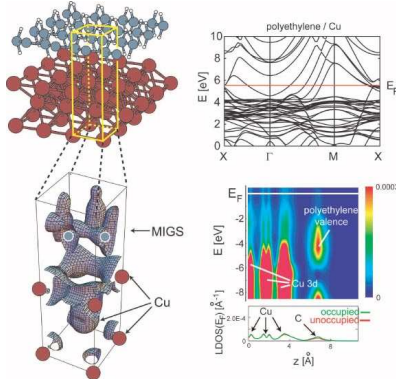

FIG. 2. Theoretical result for the band structure of 1 ML polyethlene/Cu(111). Top left inset is the atomic configuration considered here, where Cu is in red, C in grey, and H in white. Bottom left is a contour plot of the local density of states (LDOS), while the bottom right is the LDOS integrated over the xy plane as a function of the growth direction z and energy (color coded) along with the LDOS at E_F versus z.
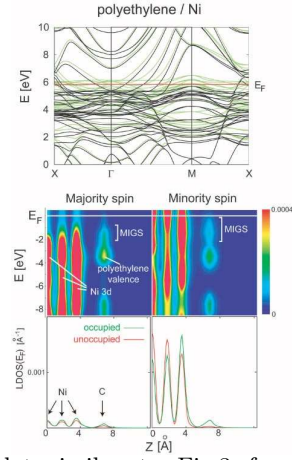

FIG. 3. A plot similar to Fig.3 for 1 ML polyethylene/Ni(111), where the spin density functional theory is adopted. Green (black) lines in the band structure represent the majority (minority) spin.
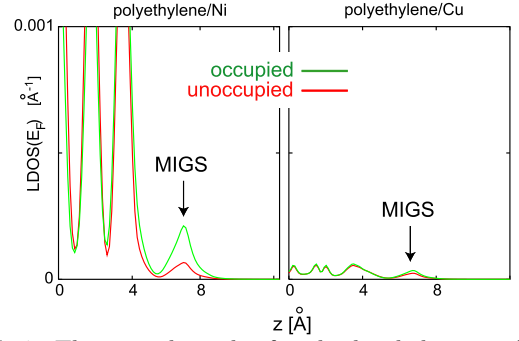

FIG. 4. Theoretical results for the local density of occupied and unoccupied states at E_F are compared for polyethylene/Ni and polyethylene/Cu.
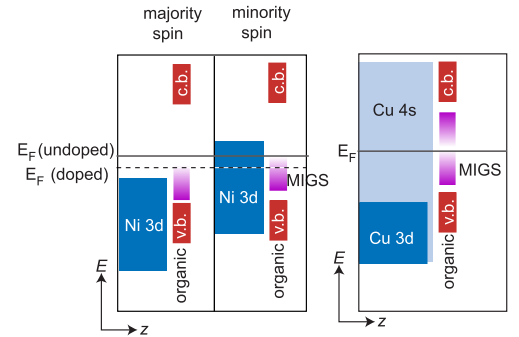

FIG. 5. A schematic energy diagram for MIGS in organic/Ni and in organic/Cu.